Micro-canonical Statistical Mechanics of some Non-Extensive Systems *

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Non-extensive systems do not allow to go to the thermodynamic limit. Therefore we have to reformulate statistical mechanics without invoking the thermodynamical limit. I.e. we have to go back to Pre-Gibbsian times. We show that Boltzmann's mechanical definition of entropy S as function of the conserved "extensive" variables energy E, particle number N etc. allows to describe even the most sophisticated cases of phase transitions unambiguously for "small" systems like nuclei, atomic clusters, and selfgravitating astrophysical systems: The rich topology of the curvature of $S(E, N)$ shows the whole "Zoo" of transitions: transitions of 1.order including the surface tension at phase-separation, continuous transitions, critical and multi-critical points. The transitions are the "catastrophes" of the Laplace transform from the "extensive" to the "intensive" variables. Moreover, this classification of phase transitions is much more natural than the Yang-Lee criterion.

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I. INTRODUCTION

This conference is addressed to the extension of thermo-statistics to non-extensive systems. This is a new realm of thermo-statistics which came into focus by the pioneering work of Tsallis [1]. Non-extensive systems are defined by the following property: If they are divided into pieces, their energy and entropy is not the sum of the energies and entropies of their parts in contrast to conventional extensive systems where this is assumed at least if the pieces are themselves macroscopic. This is the case if the forces in the systems have a long range comparable with or larger than the linear dimensions of the system like for nuclei, atomic clusters and astrophysical objects. However, also inhomogeneous systems, e.g. systems with separated phases are non-extensive.

Although the largest possible systems like clusters of galaxies belong to this group I call these systems "small" to stress the fact that the thermodynamic limit either does not exist or makes no sense. For systems with short range forces does the entropy of the surfaces separating the different phases not scale with the volume of the system. The entropy per particle $s = S(E)/N$ shows a convex intruder with a depth $\propto N^{-1/3}$. As long as one cares about this non-concavity also these systems are to be considered as non-extensive.

Elliot Lieb, Boltzmann laureate from 1998, claims [2,3] " Extensivity is essential for thermodynamics to work !" This is certainly true for the original statistical foundation of thermodynamics by Gibbs [4]. For the extension of thermo-statistics to non-extensive, "small" systems one should, however, remember that the original formulation by Boltzmann, even though he did presumably not think of non-extensive systems, does not rely on the use of the thermodynamic limit nor any assumption of extensivity and concavity of the entropy, see below. Hence, before introducing any major deviation from standard equilibrium statistics one should explore its original and fundamental Boltzmann, or micro-canonical, form.

This is what I will do in the following and demonstrate that Lieb's claim is wrong and contradicts to Boltzmann's view of thermodynamics. *Entropy as defined by Boltzmann does not invoke the thermodynamic limit and, consequently, does not demand extensivity.* Moreover, it will even turn out that the non-extensivity of inhomogeneous systems with separated phases gives just a clou to illuminate the physics of phase transitions explicitly and sharply. There is a huge world of non-extensive systems which can only be described by Boltzmann's micro-canonical ensemble

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written in its most condensed form on the epitaph of his gravestone which covers all equilibrium thermodynamics:

$$\boxed{S = k * lnW}$$

where

$$W(E, N, V) = \epsilon_0 tr\delta(E - H_N) \tag{1}$$
$$tr\delta(E - H_N) = \int \frac{d^{3N}p \, d^{3N}q}{N!(2\pi\hbar)^{3N}}\delta(E - H_N).$$

is the volume of the $3N - 1$ dimensional manifold at given sharp energy, the micro-canonical ensemble. (ϵ_0 is a suitable small energy constant to make the W dimensionless.)

In his famous book "Elementary Principles in Statistical Physics" Gibbs deduced the canonical ensemble from the fundamental micro-canonical. He showed that the canonical one becomes equivalent to the micro-canonical ensemble *in the thermodynamic limit if the system is homogeneous.* Otherwise, the canonical and grand-canonical are not correct. On page 75, chapter VII of [5] he gives explicitly the example of the separation of the liquid and gas phase for which the canonical fluctuations of the energy per particle do not vanish even in the thermodynamic limit and the canonical ensemble, and with it the "Boltzmann-Gibbs" distribution loose their validity. The reason for the special fundamental role of the micro ensemble comes of course from the fact that the internal dynamics of a many-body system conserves energy and does not mix different energy shells. In an open system embedded in a heat bath the mechanism of energy violation operates via the surface between the system and the bath and is of the same order in the particle number $\propto N^{2/3}$ as any other internal surface energies, which are also to be ignored in the canonical treatment.

Boltzmann defines the entropy in eq.(1) as a measure of the mechanical N-body phase space. Thermodynamics has thus a *geometrical interpretation* and can be read off from the *topology* of $W(E, N, \cdots)$, the volume of its constant energy manifold. No probabilistic interpretation must be invoked like

$$S = -\sum_i p_i \ln p_i, \tag{2}$$

where p_i is the probability to find the N-particle configuration i in the ensemble.

This form of entropy can be investigated for any finite even "small" system without any reference to the thermodynamic limit. I will show here that all thermodynamical features of such a system including the whole "zoo" of phase transitions and critical phenomena can be read off from this topology. This proves that in contrast to what is written in most textbooks of statistical mechanics *phase transitions do exist and can be sharply defined in finite even "small" and non-extensive systems.*

Conventional thermo-statistics, however, relies heavily on the use of the thermodynamic limit $(V \to \infty|_{N/V, \text{ or } \nu \text{ const.}})$ and extensivity, c.f. e.g. the book of Pathria [7]. This is certainly not allowed for our systems. That the *micro-canonical* statistics works well also for "small" systems without invoking extensivity will be demonstrated here for finite normal systems which are also non-extensive at phase transitions of first order. The use of the thermodynamic limit and of extensivity, however, is closely intervowen with the development of thermodynamics and statistical mechanics since its beginning more than hundred years ago. When we extend thermodynamics to "small" systems we should establish the formalism of thermodynamics starting from mechanics in order to remain on a firm basis. We will see how this idea guides us to more and deeper insight into the most dramatic phenomena of thermodynamics, phase transitions. Moreover, it gives the most natural extension of thermo-statistics to many non-extensive systems without invoking any modification of the entropy like that proposed by Tsallis [1]. This discussion may further help to illuminate the domain of physical situations where the Tsallis formalism is relevant: systems that do not populate the energy manifold of phase space densely perhaps in a fractal way, perhaps at the edge of chaos c.f. [8].

I will sketch a deduction of thermo-statistics from the principles of mechanics alone. Nothing outside of mechanics must be invoked. This was the starting point of Boltzmann [9] , Gibbs [5], Einstein [10,11] and the Ehrenfests [12,13] at the beginning of the last century. They all agreed on the logical hierarchy of the micro-canonical as the most fundamental ensemble from which the canonical, and grand-canonical ensembles can be deduced under certain conditions. According to Gibbs the latter two approximate the micro ensemble in the thermodynamic limit of infinitely many particles interacting by short range interactions if the system is homogeneous. Then surface effects and fluctuations can be ignored relatively to the bulk mean values. This is the main reason why the thermodynamic limit became basic in the statistical foundation of macroscopic thermodynamics. However, it was Gibbs [6] who stressed that the equivalence of the three ensembles is not true at phase transitions of first order, even in the thermodynamic limit.

The link between the micro and the grand ensemble is established by the double Laplace transform:

$$Z(T,\nu,V) = \iint_0^\infty \frac{dE}{\epsilon_0}\, dN\; e^{-[E/T+\nu N-S(E)]} = \frac{V^2}{\epsilon_0} \iint_0^\infty de\, dn\; e^{-V[e/T+\nu n-s(e,n)]} \tag{3}$$

Globally $s(e,n) = S(e = E/V, n = N/V)/V$ is concave (downwards bended). If $s(e,n)$ is also locally concave then there is a single point e_s,n_s for given T,ν as shown in figure (1) with

$$\frac{1}{T} = \beta = \left.\frac{\partial S}{\partial E}\right|_s \tag{4}$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_s \tag{5}$$

$$\nu = -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_s, \tag{6}$$

and a one to one mapping is generated by the Laplace transform eq.(3) from the micro variables E, N to the grand canonical T,ν. This is illustrated by figure (1) for the case of a single conserved variable E.
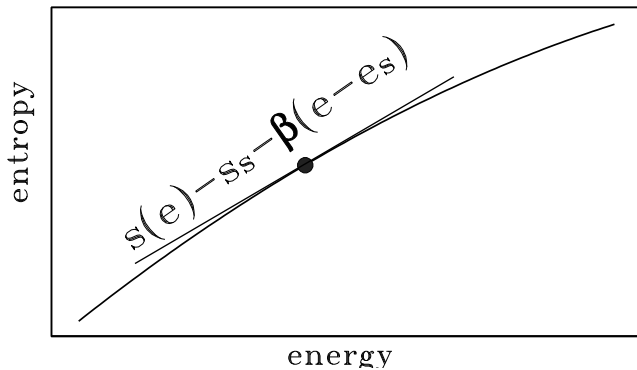

FIG. 1. Concave $s(e)$ touching the tangent with slope β at a single stationary point.

In Gaussian approximation $s(e)$ remains under the tangent line and in the thermodynamic limit $(V \to \infty)$ only the immediate neighborhood of the stationary point contributes. The importance of the curvature of $s(e)$ for the bijective mapping is evident.

An equilibrated many-body system is characterized by few macroscopic quantities:

1. Its energy E, mass (number of atoms) N, volume V,

2. its entropy S eq.(1),

3. its temperature T eq.(4), pressure P eq.(5), and chemical potential ν eq.(6).

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There are important qualitative differences between these three groups: All variables of the first group have a clear mechanical significance. They are conserved and well defined at each point of the N-body phase space. The internal dynamics of the system cannot leave the shell in phase space which is defined by these variables. Also entropy as the most important quantity within thermodynamics has with eq.(1) a clear mechanical foundation since Boltzmann. The set of points on this surface defines the micro-canonical ensemble. In contrast to the conserved quantities which are defined at each phase space point, entropy refers to the whole micro-canonical ensemble.

Remark: For a system with discrete energies E_i with some degeneration $n(E_i)$ e.g. a lattice or a quantum system one should define the micro-canonical partition sum by the number $W = n(E_i)$ of states at this energy. When we discuss derivatives of W we imagine a suitable smoothing of this.

It is important to notice that Boltzmann's and also Einstein's formulation allows for *defining the entropy entirely within mechanics* by $S_{micro} := ln[W(E, N, V)]$. *It is a single valued, non-singular, in the classical case multiply differentiable function of all "extensive", conserved dynamical variables.* No thermodynamic limit must be invoked and this definition applies to non-extensive like our "small" systems as well.

The third group of quantities which characterize the thermodynamical state of an equilibrated many-body system, temperature T, pressure P and chemical potential ν have no immediate mechanical significance. From the mechanical point of view they are secondary, derived quantities. This difference to the two other groups of variables will turn out to be significant for "small" systems. Again, like entropy itself, these quantities refer to the whole micro-canonical ensemble, not to an individual point in the N-body phase space.

Starting from this point, the conventional thermo-statistics assumes extensivity and explores the thermodynamic limit ($V \to \infty|_{N/V, \text{ or } \nu \text{ const.}}$) c.f. [7]. This procedure follows Gibbs [5]. He introduced the canonical ensemble, which since then became the basic of all modern thermo-statistics.

II. PHASE TRANSITIONS MICRO-CANONICALLY

This talk addresses phase transitions in "small" systems. Conventionally phase transitions are thought to exist only in the thermodynamic limit ($V \to \infty|_{N/V, \text{ or } \nu \text{ const.}}$). Yang and Lee [14] define them by the singularities of the grand-canonical partition sum as function of the fugacity $z = e^{\nu}$. As the partition sum $Z(T, \nu)$ is analytical in z for finite volumes V the singularities can occur in the thermodynamic limit only ($V \to \infty|_{e,n}$). I will show how these singularities arise from points in the parameter space $\{e, n, \cdots\}$ where the micro-canonical (Boltzmann) entropy $s(e, n)$ has either vanishing or even positive curvature. These are the catastrophes of the Laplace transform from the micro-canonical to the grand-canonical partition sum (3).

At phase transitions the inter-phase surface does not scale with the volume. Systems with phase separation are non-extensive. These configurations become exponentially suppressed in the canonical ensemble [6]. Moreover, Schrödinger thought that Boltzmann's entropy is not usefull to describe systems other than gases [15]. However, today with the powerfull and cheap computers we can explore the micro-canonical ensemble in realistic situation. The clarification the basic role of Boltzmann's statistics in the most dramatic situations of equilibrium thermodynamics is demanding. To realize the powerful application of Boltzmann's [not Boltzmann-Gibbs (!)] statistics to non-extensive, finite systems having a non-concave entropy $s(e, n, \cdots)$ may also specify the cases where one has to go beyond and where a generalization like Tsallis entropy is needed.

When there are no singularities in the partition sum $Z(T, \nu)$ for finite systems, are there no phase transitions in finite systems? There are phenomena observed in finite systems which are typical for phase transitions. Sometimes this is even so in astonishingly small systems like nuclei and atomic clusters of ~ 100 atoms [16–18]. In chapter (IV) and in reference [19] we show that their characteristic parameters as transition temperature, latent heat, and *surface tension* are – in the case of some metals – already for thousand atoms close, though of course not equal, to their known bulk values. Therefore, it seems to be fully justified to speak in these cases of phase transitions of first order.

We need an extension of thermodynamics to "small" systems which avoids the thermodynamic limit. However, here is a severe problem: *The non-equivalence of the three popular ensembles, the micro-canonical, the canonical, and the grand-canonical ensembles for "small" systems.* The energy *per particle* fluctuates around its mean value $<E/N>$ in the (grand-)canonical ensemble whereas the energy fluctuations are zero in the micro-canonical ensemble. Moreover, the heat capacity is strictly positive in the canonical ensembles whereas it may become *negative* in the micro ensemble. To extend themodynamics to "small" systems it is certainly advisable to keep close contact with mechanics. It is helpful to realize that the fundamental micro-canonical ensemble as introduced by Boltzmann is the only one which has a clear mechanical definition [20,11] for finite systems.

To extend the definition of phase transitions of Yang and Lee to finite systems we must study which feature of the micro-canonical partition sum $W(E, N, V)$ leads to singularities of the grand-canonical potentials $\frac{1}{V}ln[Z]$ as function of $z = e^\nu$ by the Laplace transform eq.(3). In the thermo-dynamic limit $V \to \infty|_{\nu \text{ const.}}$ this integral can be evaluated by asymptotic methods as discussed above. If there is only a single stationary point then there is a one to one mapping of the grand-canonical ensemble to the micro-canonical one and energy-fluctuations disappear $\propto 1/\sqrt{N}$.

This, however, is not the case at phase transitions of first order. Here the grand-canonical en-semble contains several Gibbs states (stationary points, c.f. the figure (6)) at the same temperature and chemical potential which contribute similarly to the integral eq.(3). The statistical fluctuations of e and n do not disappear in the grand-canonical ensemble even in the thermodynamic limit. Between the stationary points $s(e, n)$ *has at least one principal curvature* ≥ 0. Here van Hove's concavity condition [21] for the entropy $s(e, n)$ is violated. In the thermodynamic limit these points get jumped over by the integral (3) and $ln[Z]$ becomes non-analytic. Consequently, we *define phase transitions also for finite systems topologically by the points and regions of non-negative curvature of the entropy surface $s(e, n)$ as a function of the mechanical, conserved "extensive" quantities like energy, mass, angular momentum etc..*

The central quantity of our further discussion, the determinant of the curvatures of $s(e, n) = S(e = E/V, n = N/V)/V$ is defined as

$$d(e, n) = \left\| \begin{matrix} \frac{\partial^2 s}{\partial \epsilon^2} & \frac{\partial^2 s}{\partial n \partial e} \\ \frac{\partial^2 s}{\partial e \partial n} & \frac{\partial^2 s}{\partial n^2} \end{matrix} \right\| = \left\| \begin{matrix} s_{ee} & s_{en} \\ s_{ne} & s_{nn} \end{matrix} \right\| = \lambda_1 \lambda_2. \tag{7}$$

The two curvature eigenvalues (main curvatures) are assumed to be ordered and $\lambda_1 > \lambda_2 < 0$.

Also critical fluctuations, i.e. abnormally large fluctuations of some extensive variable in the grand-canonical ensemble or the eventual divergence of some susceptibilities are micro-canonically connected to the vanishing of the curvature determinant, e.g. in the following examples of $d(e, n)$ or $d(e, m)$ respectively:

The micro-canonical specific heat is given by :

$$c_{micro}(e, n) = \left. \frac{\partial e}{\partial T} \right|_\nu = -\frac{s_{nn}}{T^2 d(e, n)} , \tag{8}$$

$$d = \frac{d(\beta\nu)}{d(en)} \tag{9}$$

or the isothermal magnetic susceptibility by :

$$\chi_{micro, T}(e, m) = \left. \frac{\partial m}{\partial B} \right|_T = \frac{s_{ee}}{d(e, m)} , \tag{10}$$

$$\text{with } s_{ee} = \frac{\partial^2 s}{\partial e \partial e} \text{ etc.} \tag{11}$$

In the case of a classical continuous system $s(e, n)$ is everywhere finite and multiply differentiable. In that case the inverse susceptibilities $[c_{micro}(e, n, V)]^{-1}$ and $[\chi_{micro, T}(e, m, V)]^{-1}$ are well be-haved smooth functions of their arguments even at phase transitions. Problems arise only if the susceptibilities are considered as functions of the "intensive" variables T, and ν or $B \propto \partial S/\partial m$ [22]. In the case of lattice systems we can only assume that the inverse susceptibilities are similarly well behaved.

Experimentally one identifies phase transitions of first order of course not by the non-analyticities of $\frac{1}{V}ln[Z]$ but by the interfaces separating coexisting phases, e.g. liquid and gas, i.e. by the

inhomogeneities of the system which become suppressed in the thermodynamic limit in the grand-canonical ensemble. This fact was early realized by Gibbs [23] and he emphasized that using S vs. volume, or density, at phase separation "has a substantial advantage over any other method (e.g. pressure) because it shows the region of simultaneous coexistence of the vapor, liquid, and solid phases of a substance, a region which reduces to a point in the more usual pressure-temperature plane." That is also the reason why for the grand-canonical ensemble the more mathematical definition of phase transitions [14] is needed. The main advantage of the micro-canonical ensemble is that it allows for *inhomogeneities* as well and thus we can keep much closer to the experimental criteria for finding phase transitions.

Interfaces have three opposing effects on the entropy:

- An entropic *gain* by putting a part (N_1) of the system from the majority phase (e.g. solid) into the minority phase (bubbles, e.g. gas) with a higher entropy per particle. However, this has to be paid by additional energy ΔE to break the bonds in the "gas"-phase. As both effects are proportional to the number of particles N_1 being converted, this part of the entropy rises linearly with the additional energy.

- With rising size of the bubbles their surfaces grow. This is connected to an entropic *loss* due to additional correlations between the particles at the interface(surface entropy) proportional to the interface area. As the number of surface atoms is $\propto N_1^{2/3}$ this is not linear in ΔE and leads to a convex intruder in $S(E, N, V)$, the origin of surface tension [24]. This is also the reason why systems with phase separation are non-extensive c.f. chapter (VI).

- An additional mixing entropy for distributing the N_1-particles in various ways over the bubbles.

At a (multi-) critical point two (or more) phases become indistinguishable because the interface entropy (surface tension) and with it the inhomogeneity (interface) disappears.

In order to demonstrate this we investigate in the following the 3-states diluted Potts model now on a *finite* 2-dim (here $L^2 = 50^2$) lattice with periodic boundaries in order to minimize effects of the external surfaces of the system. The model is defined by the Hamiltonian:

$$H = - \sum_{i,j}^{n.n.pairs} o_i o_j \delta_{\sigma_i, \sigma_j} \tag{12}$$

$$n = L^{-2} N = L^{-2} \sum_i o_i.$$

Each lattice site i is either occupied by a particle with spin $\sigma_i = 1, 2$, or 3 or empty (vacancy). The sum is over neighboring lattice sites i, j, and the occupation numbers are:

$$o_i = \begin{cases} 1 & \text{, spin particle in site } i \\ 0 & \text{, vacancy in site } i \end{cases}. \tag{13}$$

This model is an extension of the ordinary ($q = 3$)-Potts model to allow also for vacancies. At zero concentration of vacancies ($n = 1$), the system has in the limit of infinite volume V a continuous phase transition at $e_c = 1 + \frac{1}{\sqrt{q}} \approx 1.58$ [25,7]. With rising number of vacancies the probability to find a pair of particles at neighboring sites with the same spin orientation decreases. The inclusion of vacancies has the effect of an increasing effective $q_{eff} \geq 3$. This results in an increase of the critical energy of the continuous phase transition with decreasing n and provides a line of continuous transition, which is supposed to terminate when q_{eff} becomes larger than 4, where the transition becomes first order.

At smaller energies the system is in one of three ordered phases (spins predominantly parallel in one of the three possible directions). We call this the "solid" phase. This scenario gets full support by our numerical findings.

In figure (2) the determinant of curvatures of $s(e, n)$:

$$d(e, n) = \left\| \begin{matrix} \frac{\partial^2 s}{\partial e^2} & \frac{\partial^2 s}{\partial n \partial e} \\ \frac{\partial^2 s}{\partial e \partial n} & \frac{\partial^2 s}{\partial n^2} \end{matrix} \right\| = \left\| \begin{matrix} s_{ee} & s_{en} \\ s_{ne} & s_{nn} \end{matrix} \right\| = \lambda_1 \lambda_2 \tag{14}$$

is shown. On the diagonal we have the ground-state of the 2-dim Potts lattice-gas with $e_0 = -2n$, the upper-right end is the complete random configuration (here without contour lines), with the maximum allowed excitation $e_{rand} = -\frac{2n^2}{q}$ and the maximum possible entropy. In the region above the line $\widehat{CP_mB}$ we have the disordered, "gas". Here the entropy $s(e,n)$ is concave ($d > 0$), both curvatures are negative (we have always the smaller one $\lambda_2 < 0$). This is also the case inside the triangle AP_mC (ordered, "solid" phase). In these regions the Laplace integral eq.(3) has a single stationary point. They correspond to pure phases.
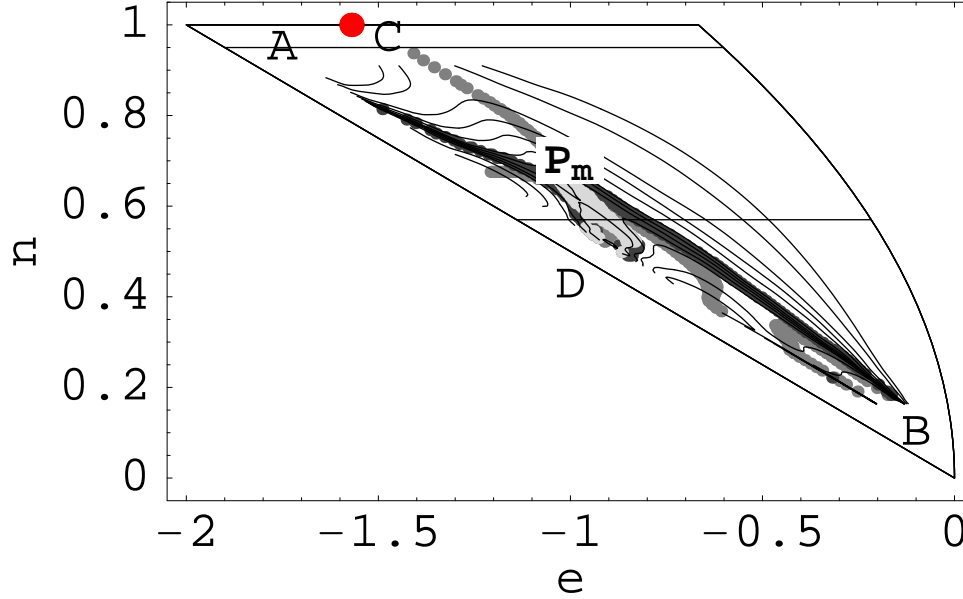

FIG. 2. Contour plot of the determinant of curvatures $d(e,n)$ defined in eq.(14).The grey/black strips separate: regions above $\widehat{CP_mB}$: concave, $d > 0$, pure phase (disordered, gas), in the triangle AP_mC concave, pure phase (ordered, solid); below $\widehat{AP_mB}$: convex, $d < 0$, phase-separation, first order; at the dark lines $\widehat{AP_mB}$ we have $d(e,n) = 0$: termination or border lines of the first order transition; medium dark lines e.g $\widehat{CP_m}$: $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$; here the curvature determinant has a minimum in the direction of the largest curvature eigenvector $\mathbf{v}_1$; in the cross-region (light grey) we have: $d = 0 \wedge \boldsymbol{\nabla} d = \mathbf{0}$ this is the locus of the multi-critical point P_m where the larger curvature $\lambda_1 \equiv 0$ and $s(e,n)$ is cylindrical up to at least third order in Δe and Δn. The two horizontal lines give the positions of the two cuts shown in figs.3,4.
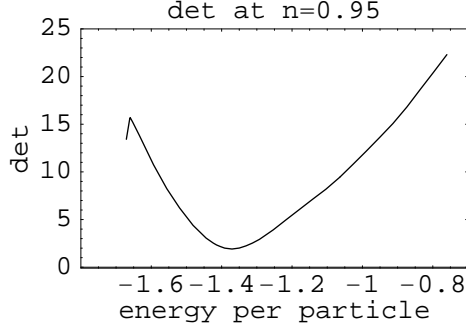
FIG. 3. Cut through the determinant $d(e,n)$ along the upper line shown in figure (2) at const. $n = 0.95$, through the critical line $\widehat{CP_m}$ close to the critical point C of the ordinary Potts model $(n \sim 1)$
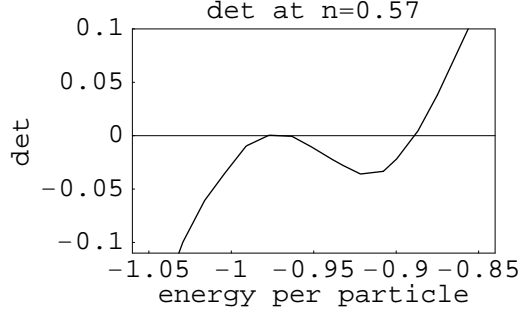
FIG. 4. Cut through the determinant $d(e,n)$ along the line shown in figure (2) at const. $n = 0.57$, slightly below the multi-critical region. There are several zero points of the determinant of curvatures: The left one is simultaneously a maximum with $\boldsymbol{\nabla} d = \mathbf{0}$ and consequently critical as discussed above

Below $\widehat{AP_mB}$ $s(e,n)$ is convex $(d < 0)$ corresponding to phase-separation, first order. At these $\{e,n\}$ the Laplace integral (3) has no stationary point. Here we have a separation into coexisting phases, e.g. solid and gas. Due to the inter-phase surface tension or the negative contribution to the entropy by the additional correlations at the phase boundaries (surfaces), $s(e,n)$ has a *convex* intruder with positive largest curvature. In [26,27,24,19] it is shown that the depth of the convex intruder in $s(e,n)$ gives the surface tension, c.f. chapter (IV). At the dark lines like $\widehat{AP_mB}$ we have $d(e,n) = 0$. These are the termination lines of the first order transition. At these lines one of the two phases is depleted and beyond all particles are in the other phase (solid or gas respectively).

Along the medium dark lines like $\widehat{P_mC}$ we have $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$, here the curvature determinant has a minimum in the direction of the largest curvature eigenvector $\mathbf{v}_1$. The line $\widehat{P_mC}$ towards the critical point of the ordinary $(q = 3)$-Potts model at $e = -1.58$, $n = 1$ correponds to a critical line of second order transition which terminates at the multicritical "point" P_m. It is *a deep valley* in $d(e,n)$ c.f. fig.3 which rises slightly up towards C. On the level of the present simulation we cannot decide whether this rise is due to our still finite, though otherwise sufficient, precision or is a general feature of finite size. (The largest curvature λ_1 of $s(e,n)$ has a local *maximum* with $\lambda_1 \overset{<}{\sim} 0$, or $d \overset{>}{\sim} 0$). Because of our finite interpolation width of $\Delta e \sim \pm 0.04$, $\Delta n \sim \pm 0.02$ it might be that this valley of $d(e,n)$ gets a little bit filled up from its sides and the minimum of $d(e,n)$ is rounded, c.f. fig.3. The valley converts below the crossing point P_m into *a flat ridge* inside the convex intruder of the first order lattice-gas phase-separation region see e.g. fig.(4).

In the cross-region (light grey in fig.2) we have: $d = 0 \wedge \boldsymbol{\nabla} d = \mathbf{0}$. This is the locus of the multi-critical point P_m where the large curvature $\lambda_1 \equiv 0$ in a *two-dimensional* neighborhood. Here the curvature determinant $d(e,n)$ is flat up to at least second order in both directions Δe and Δn and $s(e,n)$ is cylindrical. It is at $e_m \sim -1$, $n_m \sim 0.6$ or $\beta_m = 1.48 \pm 0.03$, $\nu_m = 2.67 \pm 0.02$. Naturally, P_m spans a much broader region in $\{e,n\}$ than in $\{\beta,\nu\}$, remember $d(e,n)$ is *flat* near P_m. This situation reminds very much the well known phase diagram of a $^3\mathrm{He}$ –$^4\mathrm{He}$ mixture in temperature vs. mole fraction of $^3\mathrm{He}$ c.f. fig.3. in ref. [28].

III. ON THE TOPOLOGY OF CURVATURES

The two eigenvalues of the curvature matrix (14) are:

$$\lambda_{1,2} = \frac{s_{ee} + s_{nn}}{2} \pm \frac{1}{2}\sqrt{(s_{ee} + s_{nn})^2 - 4d} \tag{15}$$

and the corresponding eigenvectors are :

$$\mathbf{v}_\lambda = \frac{1}{\sqrt{(s_{ee} - \lambda)^2 + s_{en}^2}} \begin{pmatrix} -s_{en} \\ s_{ee} - \lambda \end{pmatrix}. \tag{16}$$

$$\tag{17}$$

At critical points the following conditions hold:

$$d = -\frac{\partial(\beta\nu)}{\partial(en)} = L^2 D = 0 \tag{18}$$

$$s_{ee}s_{nn} = s_{en}^2. \tag{19}$$

Here the directions β =const. and ν = const. are *parallel,* $\qquad\qquad$ (20)

the Jacobian vanishes and we have :

$$\left.\frac{\partial\beta}{\partial e}\right|_\nu = \frac{d}{s_{nn}} = 0 \tag{21}$$

$$\left.\frac{\partial\nu}{\partial n}\right|_\beta = \frac{-d}{s_{ee}} = 0. \tag{22}$$

$$\lambda_1 = 0 \tag{23}$$

$$\lambda_2 = s_{ee} + s_{nn} \tag{24}$$

$$\mathbf{v}_{\lambda=0} = \frac{1}{\sqrt{s_{ee}^2 + s_{en}^2}}\begin{pmatrix} -s_{en} \\ s_{ee} \end{pmatrix} \tag{25}$$

$$\mathbf{v}_{\lambda\leq 0} = \frac{1}{\sqrt{s_{nn}^2 + s_{en}^2}}\begin{pmatrix} s_{en} \\ s_{nn} \end{pmatrix}. \tag{26}$$

The vanishing of d alone is not sufficient for criticality. Physically, it means that the surface entropy (tension) and with it the interface separating coexistent phases disappears. This, however, can also signalize a depletion of one of the two phases in favor of the other. At a critical end-point, however, the interface disappears at a non vanishing number of atoms in each of the two phases. I.e. in an infinitesimal neighborhood of a critical point, d must remain zero. In a topologically formulation a critical end-point of first order transition is at:

$$d = 0 \tag{27}$$

$$and$$

$$\mathbf{v}_1 \cdot \boldsymbol{\nabla}d = 0, \tag{28}$$

whereas at a multi-critical point we have $\boldsymbol{\nabla d} = \mathbf{0}$.

This is a generalization of the well known condition for a continuous transition in one dimension: the simultaneous vanishing of $\beta'(e) = 0$ and of the curvature of $\beta(e)$, $\beta''(e) = 0$.

Figure (5) shows a map of some trajectories which follow the eigen-vector $\boldsymbol{v_1}$ with the largest curvature eigen-value λ_1. In the region of the convex intruder ($\lambda_1 > 0$) i.e. the region of phase-separation $\boldsymbol{v_1}$ is $\sim$ parallel to the ground state $e = -2n$. Also the lines of β =const. and ν =const. follow approximately this direction. Their Jacobian $\partial(\beta\nu)/\partial(en) = d(e, n)$ is negative but small. This reminds of the situation in the thermodynamic limit where this region of phase separation is flat $(d(e, n))$ or $s(e, n)$ cylindrical, both intensive variables are constant and the Jacobian $d \to -0$. One can also see in fig.5 how the direction of the largest curvature $\boldsymbol{v_1}$ turns into the e-direction when one approaches the critical point C of the ordinary ($q = 3$)-Potts model at $n = 1$.

At $n = 1$ we know that for an infinite system the ordinary ($n = 1$) three state Potts model has a second order transition at $e = -1.58$ where the curvature of $s(e)$ vanishes, $s_{ee} = 0$. I.e. the component $\boldsymbol{v_1} \cdot \boldsymbol{\nabla}d$ of $\boldsymbol{\nabla}d$ indicates nicely the locus of the second order "temperature driven" transition of the ordinary Potts model.
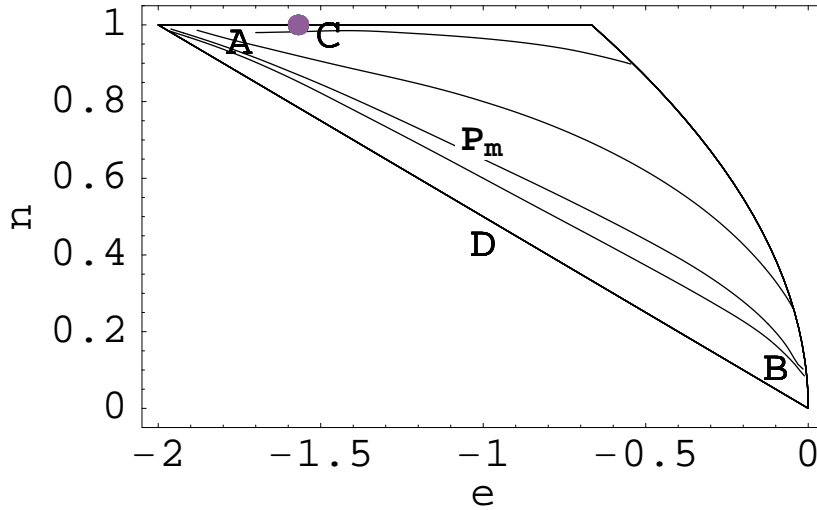
FIG. 5. Direction of the largest principal curvature $\boldsymbol{v_1}$.

This chapter was an overview on the power and extreme rich insight that the topology of curvatures of Boltzmann's micro-canonical entropy $s(e,n)$ can give in a generic case of a "small" and non-extensive system.

IV. WHAT IS THE PHYSICS BEHIND A POSITIVE CURVATURE?

It is linked to the inter-phase surface tension. This is shown in a simulation of 1000 sodium atoms at constant external pressure $P = 1$atm. In figure (6) I show the micro-canonical entropy $s(e)$ for 1000 sodium atoms with realistic interactions. Details of this calculation are given in [19]. Here only a few remarks: The calculations were done at a constant volume $V(E)$ which was chosen for the whole ensemble at the given energy so that the pressure $P = \frac{\partial S}{\partial V}/\frac{\partial S}{\partial E}$ is given to be 1 atm. The important and characteristic difference to Andersen's constant pressure ensemble [29] should be noticed! This is discussed in my book that will be published soon [30].
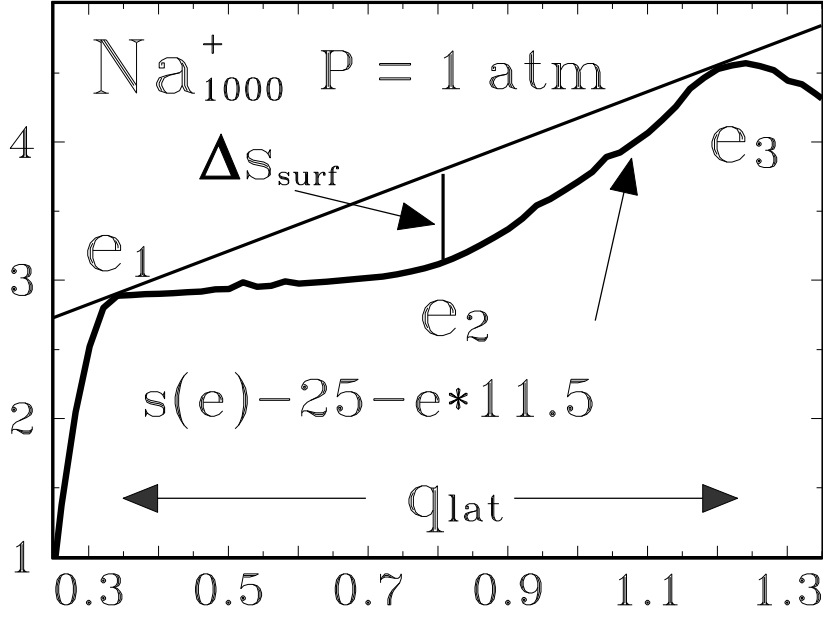
FIG. 6. Micro-canonical entropy as function of excitation energy of 1000 sodium atoms at an external pressure $P = (\partial S(E,V)/\partial V)/(\partial S/\partial E) = 1$ atm. At e_1 the system is in the liquid phase and at e_3 in the pure gas phase. Δs_{surf} gives the entropy-loss per atom due to surface correlations

The table (I) gives the 4 characteristic parameters classifying the transition of $N = 200 \cdots 3000$ Na-atoms at external pressure of 1 atm. T_{tr} is the transition temperature ($T = (\partial S/\partial E)^{-1}$) in Kelvin, $q_{lat} = e_3 - e_1$ is the the latent energy per atom, s_{boil} is the entropy gain of a single atom when converted from the liquid phase into the gas phase. Δs_{surf} is the entropy-loss per atom due to surface correlations, N_{eff} is the average number of surface atoms of all coexisting clusters, and σ is the surface tension per surface atom. These values are compared to their corresponding values of bulk sodium.

		N_0	200	1000	3000	**bulk**
Na		$T_{tr}\ [K]$	940	990	1095	**1156**
		$q_{lat}\ [eV]$	0.82	0.91	0.94	**0.923**
		s_{boil}	10.1	10.7	9.9	**9.267**
		Δs_{surf}	0.55	0.56	0.45	
		$N_{eff}^{2/3}$	39.94	98.53	186.6	∞
		σ/T_{tr}	2.75	5.68	7.07	**7.41**

TABLE I. Transition parameters for $200 \rightarrow 3000$ sodium atoms at external pressure of 1 atm.

V. THE INFORMATION LOST IN THE GRAND-CANONICAL ENSEMBLE

In this chapter I explain how and which part of the micro-canonical phase diagram is lost in the conventional canonical treatment.
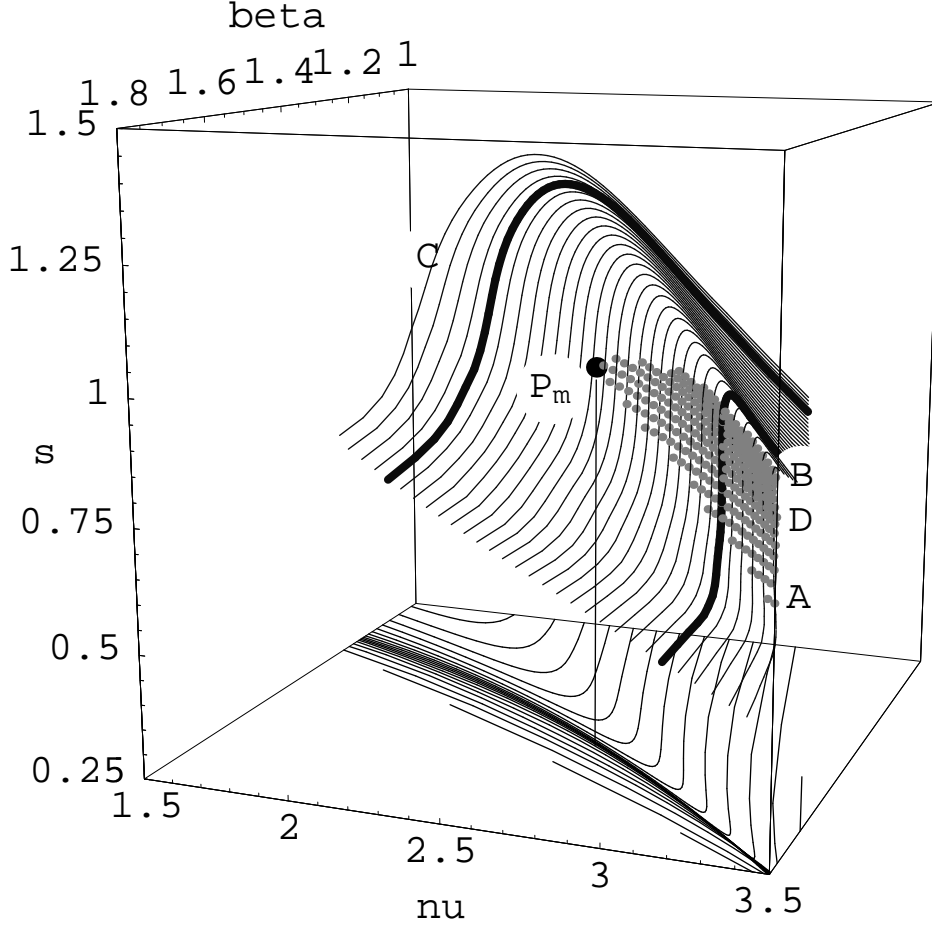

FIG. 7. Plot of the micro-canonical entropy $s_{micro}(\beta, \nu)$ as function of the "intensive" variables ($\nu = -\beta\mu$) in the figure labeled as "nu" and β is called "beta". The lines which build the surface are lines for β =const. The two bold ones indicate the cuts shown in figs.8 and 9. The positions of the points A,D,B,C defined in figure (2) are only roughly indicated. The convex intruder, the region in figure(2) below $\widehat{AP_mB}$ where we have the separation of phases and where $s_{micro}(\beta, \nu)$ becomes multi-valued as function of $\nu > \nu_{P_m}$ and $\beta > \beta_{P_m}$ is indicated by shadowing. At the bottom the projection of the entropy surface onto the $\{\beta, \nu\}$ plane is shown as contour plot. This would be all that could be seen in the conventional canonical phase-diagram. The convex part (region of phase-separation) is hidden behind the dark "critical" line.

Figure (7) explains what happens if one plots the entropy s vs. the "intensive" quantities $\beta = \partial S/\partial E$ and $\nu = \partial S/\partial N$ as one would do for the grand-canonical ensemble: As there are several points E_i, N_i with identical β, ν, $s_{micro}(\beta, \nu)$ is a multivalued function of β, ν. Here the entropy surface $s_{micro}(e, n)$ is folded onto itself. In the projection in fig.7, these points show up as a black critical line (dense region). Here this black line continues over the multi-critical point P_m towards C indicating the direction to the critical point of the ordinary $q = 3$ Potts model at $n = 1$ (zero vacancies). Between P_m and C the slopes

$$\left.\frac{\partial s}{\partial \beta}\right|_\nu = \frac{1}{d}[\beta s_{nn} - \nu s_{ne}] \qquad (29)$$

or

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$$\frac{\partial s}{\partial \nu}\bigg|_{\beta} = -\frac{1}{d}[\beta s_{en} - \nu s_{ee}] \qquad (30)$$

are negative large but finite.

The information given by the projection would be all information which can be obtained from the conventional grand-canonical entropy $s(T, \nu, V)$, if we would have calculated it from the Laplace transform, eq.(3). The shaded region will be lost.

The upper part of figure (7) shows $s_{micro}(\beta, \nu)$ in a three dimensional plot. The lines building the entropy surface are lines of equal β. The images of the points A, D, B, C defined in fig.2 are roughly indicated. The back folded branches, the convex intruder of $s(e, n)$ between the lines $\widehat{AP_mB}$ and $\widehat{ADB}$, the region of phase separation, can here be seen from the side (shadowed). It is jumped over in eq. (3) and gets consequently lost in $Z(T, \nu)$. This demonstrates the far more detailed insight into phase transitions and critical phenomena obtainable by micro-canonical thermo-statistics not accessible to the canonical treatment, c.f. the similar arguments of Gibbs [23].

In the next two figures the cross-section through $s(\beta, \nu)$ at constant β along the bold lines from fig.(7) is shown in figure (8) below the multi-critical point $\beta_m = 1.48$ and in figure (9) above it. The latter clearly shows the back-bending of $s(\beta, \nu)$.
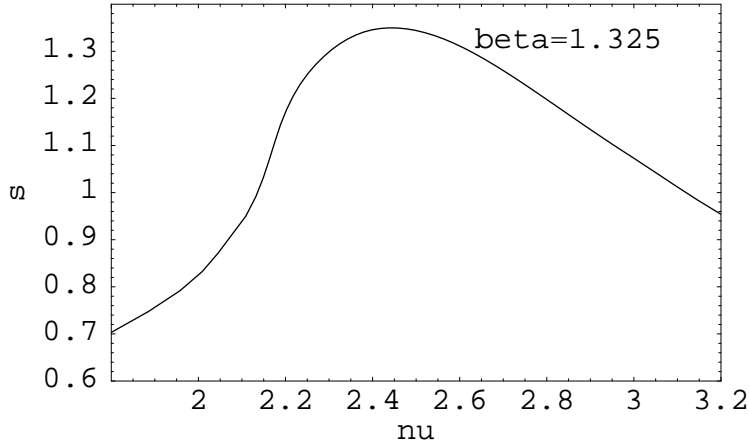

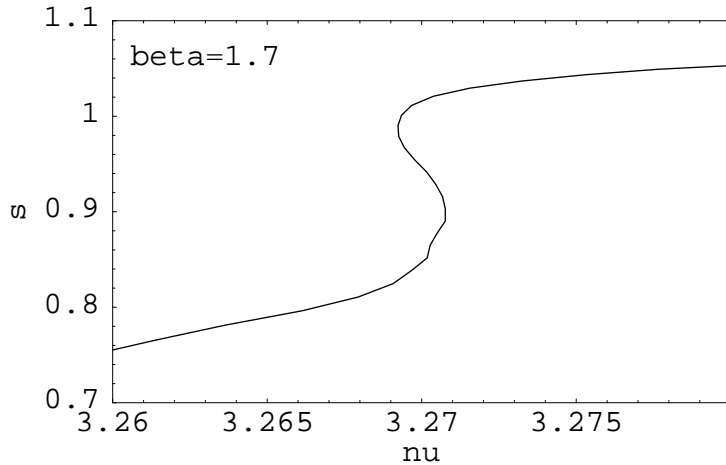FIG. 8. Plot of the entropy $s(\beta = 1.325, \nu)$

FIG. 9. Plot of the entropy $s(\beta = 1.7, \nu)$

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VI. CONVEX ENTROPY — VIOLATION OF THE SECOND LAW ?

At this point it is worth-wile to spend some words on a popular misunderstanding connected with the eventual convexity of the entropy as function of "extensive" quantities like the energy: The convex parts of $S(E, N)$ violate van Hove's concavity condition [21,31].

One may believe that this is also a contradiction to the second law of thermodynamics: At a convex region of $S(E, N)$ a split of the system into two pieces with entropies $S_1(E_1, N_1)$ and $S_2(E_2, N_2)$ would have $S_1(E_1, N_1) + S_2(E_2, N_2) > S(E_1 + E_2, N_1 + N_2)$. So the system seems to *gain* entropy by splitting.

This, however, is an error. The Boltzmann entropy as defined in eq.(1) is already the logarithm of the sum over *all* possible configurations of the system at the given energy. The split ones are a subset of these. Their partial phase space W_{split} is of course $\leq$ the total W. The entropy $S_{split} = ln(W_{split})$ is $\leq$ the total entropy. Evidently, the split system looses some surface entropy S_{surf} at the separation boundary due to additional correlations imposed on the particles at the boundary. The entropy after split is consequently:

$$S_{split} = S_1(E_1, N_1) + S_2(E_2, N_2) - S_{surf}$$
$$\leq S(E_1 + E_2, N_1 + N_2), \tag{31}$$

It is a typical finite size effect. S_{surf}/V vanishes in the limit $V \to \infty$ for interactions with *finite* range. The entropy is non-extensive for finite systems but becomes extensive in the limit, and van Hove's theorem [21] is fulfilled. This is of course only under the condition that $\lim_{V \to \infty} S_{surf}/V = 0$. So in the case of a self-gravitating system the convex intruder and the negative specific heat will not disappear [32–36].

In general this is of course a trivial conclusion: An additional constraint like an artificial cut of the system can only reduce phase space and entropy. The Second Law is automatically satisfied in the Boltzmann formalism whether S is concave or not, whether S is "extensive" or not.

A positive (wrong) curvature introduces problems to the geometrical interpretation of thermodynamics as formulated by Weinhold [37,38] which relies on the non-convexity of $S(E, N)$. Weinhold introduces a metric like

$$g_{ik} = -\frac{\partial^2 S}{\partial X^i \partial X^k} \tag{32}$$

where we identify :
$$X^1 = E$$
$$X^2 = N.$$

The thermodynamic distance is defined as :
$$\Delta_{a,b} = \sqrt{[X^i(a) - X^i(b)]g_{ik}[X^k(a) - X^k(b)]}. \tag{33}$$

Evidently, a negative metric g_{ik} is here not allowed. Of course Weinhold's theory does not apply to finite systems with phase transitions.

VII. CONCLUSION

Micro-canonical thermo-statistics describes how the entropy $s(e, n)$ as defined entirely in mechanical terms by Boltzmann depends on the conserved "extensive" variables: energy e, particle number n, angular momentum L etc. It is well defined for finite systems without invoking the thermodynamic limit. Thus in contrast to the conventional theory, we can study phase transitions also in "small" systems or other non-extensive systems. In this simulation we could classify phase transitions in a "small" system by the topological properties of the determinant of curvatures $d(e, n)$, eq.(14) of the micro-canonical entropy-surface $s(e, n)$:

In the micro-canonical ensemble of a "small", non-extensive system, phase transitions are classified unambiguously by the following topology of the curvature determinant:

- A **single stable** phase by $d(e,n) > 0$ ($\lambda_1 < 0$). Here $S(E,N)$ is concave in both directions. Then there is a one to one mapping of canonical↔micro-ensemble.
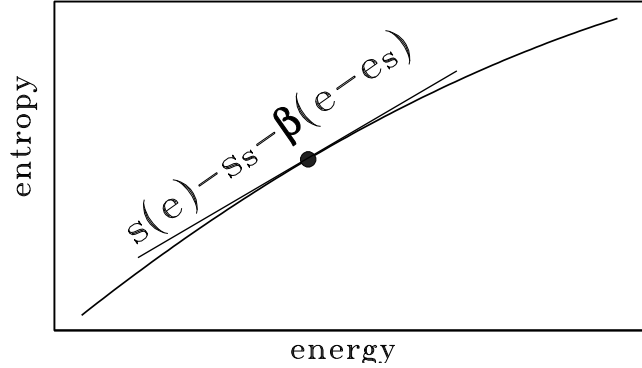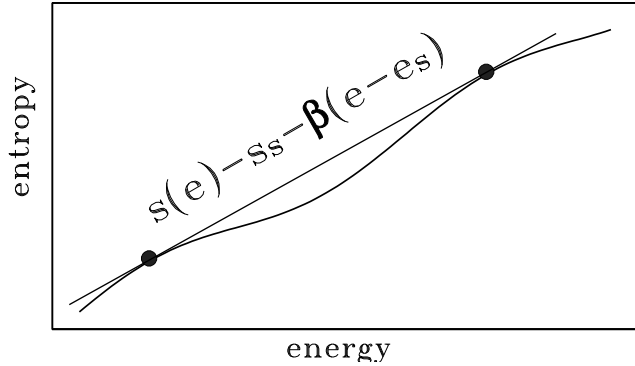

Then the last two terms in

$$\frac{F(T,\mu,V)}{V} \to e_s - \mu n_s - T s_s + T\frac{\ln\left(\sqrt{d(e_s,n_s)}\right)}{V} + o(\frac{\ln V}{V}) \tag{34}$$

can be neglected for large volume.

- A **transition of first order** with phase separation and surface tension is indicated by $d(e,n) < 0$ ($\lambda_1 > 0$). $S(E,N)$ has a convex intruder in the direction $\boldsymbol{v}_{\boldsymbol{\lambda_1}}$ of the largest curvature. Because of $d \leq 0$ the second last term in eq.(34) is complex or diverges.

The whole convex area of {e,n} is mapped into a single point in the canonical ensemble. I.e. if the curvature of $s(e,n)$ is $\lambda_1 \geq 0$ **both ensembles are not equivalent.**

- A **continuous ("second order")** transition with vanishing surface tension, where two neighboring phases become indistinguishable, is indicated by lines (critical) with $d(e,n) = 0$ and $\boldsymbol{v}_{\boldsymbol{\lambda=0}} \cdot \boldsymbol{\nabla} d = \boldsymbol{0}$. These are the catastrophes of the Laplace transform $E \to T$

- Finally a **multi-critical point** where more than two phases become indistinguishable is at the branching of several lines with $d = 0$, $\boldsymbol{\nabla} d = \boldsymbol{0}$.

Our classification of phase transitions by the topological structure of the micro-canonical Boltzmann entropy $s(e,n)$ is close to the natural experimental way to identify phase transitions of first order by the inhomogeneities at phase separation boundaries. This is possible because the micro-canonical ensemble does not suppress inhomogeneities in contrast to the grand-canonical one, as was emphasized already by Gibbs [23]. Inter-phase boundaries are reflected in "small" systems by a convex intruder in the entropy surface. With this extension of the definition of phase transitions

to "small" systems there are remarkable similarities with the transitions of the bulk. Moreover, this definition agrees with the conventional definition in the thermodynamic limit (of course, in the thermodynamic limit the largest curvature λ_1 approaches 0 from above at phase transitions of first order). The region of phase separation remains inaccessible in the conventional grand-canonical ensemble.

We believe, however, that the various kind of transitions discussed here have their immediate meaning in "small" and non-extensive systems independently whether they are the same in the thermodynamic limit (if this then exist) or not. For systems like the Potts model that have a thermodynamic limit it might well be possible that the character of the transition changes towards larger system size.

The great conceptual clarity of micro-canonical thermo-statistics compared to the grand-canonical one is clearly demonstrated. Not only that, we showed that the micro-canonical statistics gives more information about the thermodynamic behavior and more insight into the mechanism of phase transitions than the canonical ensemble: About half of the whole $\{E,N\}$ space, the intruder of $S(E,N)$ or the region between the ground state and the line $\widehat{AP_mB}$ in figure (2), gets lost in conventional grand-canonical thermodynamics. Without any doubts this contains the most sophisticated and interesting physics of this system. We emphasized this point already in [39] there, however, with still limited precision. Due to our refined simulation method [40] this could be demonstrated here with uniformly good precision in the whole $\{E, N\}$ plane. It turns out that not only are non-extensive systems a new and rich realm for thermodynamics but moreover *non-extensivity makes phase transitions much more transparant* which is no surprise as phase transitions of first order are coupled to situations where a system *prefers to become inhomogeneous, i.e. non-extensive.*

Finally, we should mention that micro-canonical thermo-statistics allowed us to compute phase transitions and especially the surface tension in realistic systems like small metal clusters [19]. Our finding [40] clearly disproves the pessimistic judgement by Schrödinger [15] who thought that Boltzmann's entropy is only usefull for gases. A recent application of micro-canonical thermo-statistics to thermodynamically unstable, collapsing systems under high angular momentum is found at [36].

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